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[TITLE OF THE INVENTION] METHOD FOR SUBSTITUTING ALUMINUM OR  
ALUMINUM ALLOY SURFACE WITH ZINC, SUBSTITUTION SOLUTION  
THEREFOR, AND ALUMINUM OR ALUMINUM ALLOY HAVING ZINC-  
15 SUBSTITUTED COAT

[ABSTRACT]

[OBJECT] To provide a zinc substitution solution, replacing  
a conventional zincate treatment solution, that gives a zinc-  
20 substituted coat with minuteness and high adhesive strength  
without adversely influencing an aluminum material being the  
object of treatment.

[SOLUTION] A zinc substitution solution for an aluminum  
material surface, being an aqueous solution for substituting  
25 an aluminum material surface with zinc, wherein the zinc

substitution solution comprises therein 1-50 g/L of a zinc compound in terms of metal zinc and 0.1-20 g/L of a fluorine compound in terms of fluorine ion, and pH thereof is 1-5; a method for substituting an aluminum material surface with zinc by using the solution; and an aluminum material having a zinc-substituted coat obtained by such a method.

[CLAIMS]

[CLAIM 1] A zinc substitution solution for an aluminum or aluminum alloy surface, being an aqueous solution for substituting an aluminum or aluminum alloy surface with zinc, wherein the zinc substitution solution comprises therein 1-50 g/L of a zinc compound in terms of metal zinc and 0.1-20 g/L of a fluorine compound in terms of fluorine, and pH thereof is 1-5.

[CLAIM 2] A zinc substitution solution according to claim 1, further comprising an aqueous salt of at least one metal selected from the group consisting of iron, nickel, copper, silver and palladium.

[CLAIM 3] A zinc substitution solution according to claim 1 or 2, further comprising an aliphatic hydroxycarboxylic acid.

[CLAIM 4] A zinc substitution solution according to any of claims 1-3, further comprising an aqueous nonionic surfactant.

[CLAIM 5] A method for substituting an aluminum or aluminum

alloy surface with zinc, wherein the aluminum or aluminum alloy and a zinc substitution solution according to any of claims 1-4 are brought into contact with each other.

[CLAIM 6] A method according to claim 5, wherein the contact is made by immersing the aluminum or aluminum alloy in a zinc substitution solution according to any of claims 1-4 for 5 seconds to 10 minutes at 5-60°C.

[CLAIM 7] A method according to claim 5 or 6, wherein the aluminum or aluminum alloy is a thin film of 5  $\mu$ m or less.

[CLAIM 8] A method according to any of claims 5-7, wherein an alkali-soluble photoresist mask is provided in advance on the aluminum or aluminum alloy surface so that the surface is partially substituted by zinc.

[CLAIM 9] Aluminum or an aluminum alloy having a zinc-substituted coat, obtained by a method according to any of claims 5-8.

[CLAIM 10] Aluminum or an aluminum alloy having a zinc-substituted coat according to claim 9, for a purpose of direct electroplating or direct electroless plating on the zinc-substituted coat.

#### [DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[FIELD OF THE INVENTION] The present invention relates to a method for substituting an aluminum or aluminum alloy surface

with zinc, a substitution solution for use in such a method, and aluminum or an aluminum alloy having a zinc-substituted coat obtained by such a method.

[0002]

5 [BACKGROUND ART] Electroplating or electroless plating directly on the surface of aluminum or an aluminum alloy is usually difficult because, for example, such a surface is easily turned non-conductive or easily corroded by an acidic or alkaline solution. It is known that even if a direct  
10 plating coat is successfully formed, the adhesiveness of the obtained coat is very low.

[0003] In view of this, new methods have been developed recently and are becoming widespread, in which the surface of aluminum, or the like, is substituted with zinc, and then  
15 subjected to electroless plating or electroplating. Such a zinc substitution treatment is commonly called a "zincate treatment", and a zinc substitution solution used therein is called a "zincate treatment solution". The zincate treatment solution generally contains 30-300 g/L of caustic soda and  
20 10-30 g/L of zinc oxide as main components, and further contains a copper salt, an iron salt, an organic amine compound, etc. As is apparent from the composition, the solution is strongly alkaline, thus presenting a disadvantage that the handling thereof may be dangerous. Moreover, in a  
25 treatment using such a solution, a significant amount of the

aluminum surface is corroded during the zinc substitution, thus detracting from the appearance of the obtained aluminum surface. Another disadvantage of the use of the zincate treatment solution is that a thin aluminum film whose thickness is about 5  $\mu\text{m}$  or less, for example, cannot be the object of treatment. Specifically, the disadvantage is that such a thin film may disappear before the zinc substitution takes place. In addition, with the conventional zincate treatment, if a patterning mask is formed by using an alkali-soluble photoresist on the aluminum surface being the object of treatment, in order to perform partial zinc substitution, the mask itself immediately falls off, thereby making desirable zinc substitution impossible.

[0004]

[PROBLEMS TO BE SOLVED BY THE INVENTION] It is an object of the present invention to replace a conventional zincate treatment solution, i.e., a strongly alkaline zinc substitution solution, by a zinc substitution solution that should be regarded as a novel zincate treatment solution capable of solving the various drawbacks set forth above of the conventional zincate treatment solution, wherein the zinc substitution solution does not substantially have adverse influence on aluminum or an aluminum alloy itself, as the object of treatment, or a photoresist, or the like, that may be formed on the surface thereof, and wherein the zinc

substitution solution has the advantage of the conventional zincate solution, i.e., being capable of giving a zinc-substituted coat with minuteness and high adhesive strength.

[0005]

5 [MEANS FOR SOLVING THE PROBLEMS] Based on the object of the invention set forth above, the present inventors have done in-depth researches to find that a solution with a particular composition and pH to be specified below can be a zinc substitution solution that fulfills the above object, that it  
10 is possible by using the zinc substitution solution to form a desirable zinc-substituted coat with good adhesive strength and minuteness on an aluminum or aluminum alloy surface through a simple operation, and that this method can suitably be applied to aluminum thin films and partial zinc  
15 substitution via a photoresist mask, thus arriving at the completion of the present invention.

[0006] The present invention provides a zinc substitution solution for an aluminum or aluminum alloy surface, being an aqueous solution for substituting an aluminum or aluminum  
20 alloy surface with zinc, wherein the zinc substitution solution comprises therein 1-50 g/L of a zinc compound in terms of metal zinc and 0.1-20 g/L of a fluorine compound in terms of fluorine (F), and pH thereof is 1-5.

[0007] Specifically, the present invention provides: a zinc  
25 substitution solution as set forth above further comprising

an aqueous salt of at least one metal selected from the group consisting of iron, nickel, copper, silver and palladium; a zinc substitution solution as set forth above further comprising an aliphatic hydroxycarboxylic acid; and a zinc substitution solution as set forth above further comprising an aqueous nonionic surfactant.

[0008] The present invention also provides a method for substituting an aluminum or aluminum alloy surface with zinc, wherein the aluminum or aluminum alloy and the zinc substitution solution of the present invention are brought into contact with each other.

[0009] Specifically, the present invention provides: a method as set forth above wherein the contact is made by immersing the aluminum or aluminum alloy in the zinc substitution solution of the present invention for 5 seconds to 10 minutes at 5-60°C; a method as set forth above wherein the aluminum or aluminum alloy is a thin film of 5  $\mu\text{m}$  or less; and a method as set forth above wherein an alkali-soluble photoresist mask is provided in advance on the aluminum or aluminum alloy surface so that the surface is partially substituted by zinc.

[0010] The present invention further provides aluminum or an aluminum alloy having a zinc-substituted coat, obtained by a method as set forth above, specifically aluminum or an aluminum alloy having the zinc-substituted coat, for a

purpose of direct electroplating or direct electroless plating on the zinc-substituted coat.

[0011]

[EMBODIMENTS OF THE INVENTION] Now, a zinc substitution  
5 solution of the present invention for substituting the surface of aluminum or an aluminum alloy (hereinafter referred to simply as an "aluminum material") with zinc will be described in detail. The solution is an aqueous solution containing predetermined amounts of a zinc compound and a  
10 fluorine compound and having pH of 1-5.

[0012] The zinc compound, being one of the essential components of the zinc substitution solution of the present invention, may be any aqueous zinc compound. Specific examples include, for example, zinc sulfate, zinc nitrate,  
15 zinc chloride, etc. Preferred among these examples is, for example, zinc sulfate, with which there is little influence on the rate at which aluminum is dissolved by the anion in an acidic range. These zinc compounds are preferably selected within such a range that the zinc metal (Zn) concentration is  
20 1-50 g/L. The concentration being lower than 1 g/L results in a disadvantage that the zinc metal substitution rate will be extremely slow, and the concentration being excessively high, above 50 g/L, results in a disadvantage that the substitution rate will be too fast, whereby the substituting  
25 zinc particles will be coarse and the adhesive strength with



the aluminum material will be low.

[0013] The fluorine compound, being the other one of the essential components of the zinc substitution solution of the present invention, serves to dissolve aluminum so that substitution thereof with zinc proceeds smoothly. Typical examples include hydrogen fluoride and ammonium hydrogen difluoride, for example, which are capable of dissolving aluminum at an appropriate rate and uniformly even when used in smaller amounts. Where ammonium hydrogen difluoride is used, the obtained solution will have desirable, appropriate pH with no pH adjustment. Instead of the fluorine compounds listed above, the present invention may also employ as the fluorine compound a fluoride salt such as lithium fluoride, sodium fluoride or potassium fluoride. When these fluoride salts are used, pH of the obtained solution may not be within the desirable acidic range, in which case a strong acid such as hydrochloric acid, sulfuric acid and nitric acid, for example, may be added separately as a pH conditioner, or hydrogen fluoride or ammonium hydrogen difluoride as mentioned above may be used additionally to achieve the desirable pH range.

[0014] These fluorine compounds are added and blended into the zinc substitution solution of the present invention within a quantity range of 0.1-20 g/L in terms of fluorine. The quantity being lower than 0.1 g/L results in a solution

with which the zinc substitution rate is too slow, and the quantity being over 20 g/L presents a disadvantage that it is necessary to add a large amount of a pH conditioner for the adjustment to the desirable pH range, which may cause a decrease in the zinc substitution rate.

[0015] It is important for the zinc substitution solution of the present invention that the pH of the solution is adjusted to be within the range of 1-5. The pH adjustment can be done by appropriately selecting the type of the zinc compound and the fluorine compound, being essential components as set forth above, or as necessary by an ordinary alkaline component addition. The alkaline component used herein for pH adjustment is not limited to any particular alkaline component. However, in order to prevent an increase in the salt concentration of the solution, it is preferred to use a strongly alkaline aqueous solution capable of desirable pH adjustment by adding only small amounts, e.g., an aqueous solution of sodium hydroxide, an aqueous solution of potassium hydroxide, an aqueous ammonia, or the like. Where the solution is excessively acidic (with pH below 1), the zinc-substituted coat may re-dissolve into the solution. The pH of the solution being over 5 presents a disadvantage that the substitution rate is too slow for practical applications, and further presents a risk that the dissolved metal may be precipitated.

[0016] With the zinc substitution solution of the present invention, various additive components may be added and blended as necessary to a basic solution, being a solution that contains as essential components a zinc compound and a fluorine compound as set forth above, in order to control (normally promote) the rate at which the aluminum material surface is substituted by zinc or to improve the minuteness, the uniformity, the smoothness, etc., of the zinc-substituted coat. Components for promoting the zinc substitution rate include, for example, an aqueous salt of at least one metal selected from the group consisting of iron, nickel, copper, silver and palladium. Examples include a chloride, a nitrate, a sulfate, and the like, of a metal mentioned above. Specific examples that are particularly preferred include ferrous chloride, nickel chloride, cuprous chloride, silver nitrate, palladium chloride, etc. These may be in the usually available hydrate form, and may be used alone or two or more of these may be used in combination. By adding an aqueous salt of such a metal by an amount such that the concentration in terms of the metal element is 0.1 ppm or more (0.0001 g/L or more), it is possible to realize the desirable effect of the addition, i.e., the effect of promoting the zinc substitution rate. Particularly, the above effect can be realized in smaller amounts if the metal is more noble than aluminum. Typically, the preferred

concentration range in terms of the metal element is about 0.1-10 ppm for silver and palladium, about 0.5-100 ppm for copper, and about 0.1-10 g/L for iron and nickel.

*would  
this form  
an alloy?*

[0017] The additive components capable of controlling the substitution rate include aliphatic hydroxycarboxylic acids. Examples include a glycolic acid, a lactic acid, a malic acid, a citric acid, a tartaric acid, for example, and these may be used alone or two or more of these may be used in combination. The amount to be added is normally preferred to be in the range of about 1-50 g/L in the present substitution solution, in which case it is possible to appropriately control the zinc substitution rate, and the precipitated zinc metal particles will be more minute.

*would  
this be  
compatible  
w/ATO  
inhibitor  
?*

[0018] Furthermore, additive components capable of improving the uniformity, the smoothness, etc., of the zinc-substituted coat include surfactants. In view of the precipitation due to the reaction between metal ions and other ions and the acid resistance, etc., aqueous nonionic surfactants are preferred among other surfactants listed above. Such aqueous nonionic surfactants include, for example, those of alkyl polyoxy ethylene ether and those of alkyl polyoxy ethylene polyoxy propylene ether. Particularly preferred among these are an ethylene oxide adduct and/or a propylene oxide adduct of alkyl phenols and higher alcohols, etc., and it is preferred that the cloudy point thereof is 40°C or more.

These may be used alone or two or more of these may be used in combination. Normally, they are added and blended in a range of about 0.1-3 g/L to the present substitution solution, whereby it is possible to improve the desirable effects, particularly the wettability to the aluminum metal surface, and to improve the uniformity of the zinc-substituted coat, thereby improving the minuteness of the zinc-substituted coat and the smoothness of the coat surface.

[0019] The zinc substitution solution of the present invention can be easily prepared by simply dissolving and mixing in water the zinc compound and the fluorine compound, as essential components, and the additive component, the pH conditioner, etc., which are added as necessary.

[0020] A method for substituting an aluminum material surface with zinc by using the zinc substitution solution of the present invention obtained as described above will now be described in detail. The aluminum material being the object of treatment may be any aluminum material as long as it has on its surface metallic aluminum that can be substituted with zinc. This accordingly includes a wide range of materials, including high-purity aluminum and aluminum alloys containing alloy components such as copper, magnesium and zinc, for example. The shape of the material is not limited to any particular shape, and it may be either an ordinary plate shape (including a thin film shape such as a film or a sheet)

or a molded material of any shape. The plate-shaped material is not limited to those of an aluminum material alone, but includes an aluminum coat (integrated with a substrate) formed by an ordinary method such as a vapor deposition method or an ion plating method on a ceramic or plastic substrate, for example.

[0021] When such an aluminum material is subjected to a treatment with the zinc substitution solution of the present invention, the aluminum material may be subjected to, as a preliminary treatment, a commonly-employed treatment such as an alkaline degreasing treatment, an etching treatment and a smut-removing treatment.

[0022] The method for the treatment with the zinc substitution solution of the present invention is not limited to any particular method as long as the solution and the aluminum material are brought into contact with each other. Most basically, the contact can be made by immersing the aluminum material in the zinc substitution solution of the present invention. Other than the immersing method, one may employ, for example, a method for spraying or applying the zinc substitution solution on the aluminum material surface.

[0023] The immersion method will be further described in detail as an example. As for the conditions for immersing the aluminum material in the zinc substitution solution of the present invention, the temperature and the immersion time

can be determined appropriately according to the composition of the solution, the desirable thickness of the zinc-substituted coat, etc. Typically, the solution temperature is appropriately selected within the range of 5-60°C depending on the composition of the solution, and the immersion time is appropriately selected within the range of about 5 seconds to 10 minutes depending on the desirable thickness. Particularly, the solution temperature for good workability is preferably within the range of about 20-40°C, i.e., around room temperature. If a temperature condition in this range is employed, it is typically preferred to employ an immersion time of about 20 seconds to 3 minutes. Thus, it is possible to form a zinc-substituted coat whose thickness is greater than or equal to 0.1  $\mu\text{m}$ , which is a desirable thickness of a zinc-substituted coat usually required for electroless plating or electroplating to be described later.

[0024] When immersing the aluminum material in the zinc substitution solution of the present invention, it is preferred to employ means such as mechanically stirring the solution, and shaking the aluminum material immersed, whereby the concentrations of zinc metal and other ions can be kept constant at the interface between the material surface and the solution, and it is therefore possible to form a more uniform zinc-substituted coat at a constant rate. The conditions under which the aluminum material and the zinc

substitution solution of the present invention are brought into contact with each other, where a method other than the immersion method is employed, may be similar to those employed in the immersion method as set forth above.

5 [0025] Particularly, with the method of the present invention, as opposed to a zincate treatment method using a conventional strongly alkaline zincate treatment solution, even if the object of treatment, as the aluminum material, is a thin aluminum film whose thickness is about 5  $\mu\text{m}$  or less,  
10 for example, the thin film will not disappear due to the strong alkalinity, and it is easily possible to perform a desirable zinc substitution treatment.

[0026] Moreover, with the method of the present invention, it is easily possible to, for example, form a patterning mask  
15 using an alkali-soluble photoresist on an aluminum surface being the object of treatment so as to partially substitute the surface with zinc, which was not possible with the conventional zincate treatment. Particularly, such partial zinc substitution can be used advantageously for forming an  
20 electric circuit on a non-conductor, for example.

[0027] Specifically, according to the present invention, this can be done by, for example, vapor-depositing aluminum to a thickness of about 0.7  $\mu\text{m}$  by an ordinary method on a ceramic molding; layering, on the formed aluminum coat, an  
25 alkali-soluble photoresist such as a dry film having an



acidic group such as a carboxyl group on the side chain;  
exposing the resist via a mask, and developping and  
patterning the same; and carrying out the method using the  
zinc substitution solution of the present invention on the  
5 obtained aluminum coat with a patterned resist to thereby  
selectively substitute only the exposed portions of the  
aluminum material surface that are not masked with the resist  
with zinc, thus partially forming a zinc coat of a desirable  
thickness. By further performing electroless nickel plating,  
10 electroless gold plating, or the like, on the obtained  
partial zinc-substituted coat, and peeling off the used  
resist and aluminum with the plating coat as a mask, it is  
possible to obtain a circuit with desirable wire bonding  
property and solder adhesiveness.

15 [0028] The thickness of the zinc-substituted coat obtained  
by the method of the present invention can be freely adjusted  
within the range of about 0.01-2.0  $\mu\text{m}$ . Moreover, the zinc-  
substituted coat is desirable in properties such as  
conductivity, and it is therefore possible to perform  
20 electroless plating or electroplating directly on the coat by  
an ordinary method.

[0029] The electroless plating may be any of various types  
of electroless plating known in the prior art, e.g., acidic  
or alkaline electroless nickel plating, alkaline electroless  
25 copper plating, etc. With the acidic electroless nickel

plating, it is possible to perform desirable nickel plating also by using a plating bath with a boric acid-based or phosphoric acid-based reducing agent, or the like. Types of electroplating that can suitably be employed include copper  
5 plating such as copper cyanide plating and copper sulfate plating, or nickel electroplating using a Watts bath, or the like. It is possible to further perform, for example, chromium electroplating, or the like, on the coat obtained by the nickel electroplating.

10 [0030] With electroless plating and electroplating as set forth above, it is possible to form a decorative metal coat on an aluminum material, and this considerably improves the corrosion resistance of aluminum. Where an aluminum thin film is used, electroless nickel plating, gold electroplating  
15 or electroless gold plating, for example, can be performed via the zinc-substituted coat of the present invention, whereby it is possible to significantly improve the conductivity of the aluminum film while ensuring adhesive strength to solder, wire bonding, etc.

20 [0031]

[EXAMPLES] Examples of the present invention will be set forth below in order to describe the present invention in greater detail. Note however that the present invention is not limited to these examples. The aluminum material to be  
25 treated in these examples is as follows, and the performance

evaluation for the zinc-substituted coat of each example was performed by a method as described below.

(1) Aluminum Material

The block-shaped aluminum material used was a JISA6063 plate material, subjected to degreasing, alkaline etching and desmutting with nitric acid.

[0032] The aluminum thin film used was a thin film obtained by vapor-depositing aluminum to a thickness of about 0.8  $\mu\text{m}$  on an alumina ceramic plate, and then degreasing the film.

(2) Evaluation Of Zinc-Substituted Coat

Various product samples having thereon zinc-substituted coats of examples of the present invention and comparative examples were further immersed in an electroless nickel-phosphorus-based plating bath ("Topnicolon BL" from Okuno Chemical Industries Co., Ltd.) for 30 minutes at 90°C to form a nickel-phosphorus plating coat having a thickness of 10  $\mu\text{m}$  on the zinc-substituted coat. Then, the appearance of each sample was visually observed to determine the presence of visible plating non-uniformity, thereby evaluating the uniformity of the zinc-substituted coat on the sample. Those without plating non-uniformity are evaluated as "(uniformity is) Present", and those with plating non-uniformity as "(uniformity is) Absent".

[0033] The adhesiveness of the zinc-substituted coat was evaluated by performing a cross-cut tape test after the

electroless nickel-phosphorus plating, in terms of the number of pieces left after the tape is peeled off divided by 100.

[0034]

[EXAMPLES 1 to 10] Zinc substitution solutions of Examples 1-10 of the present invention were prepared by dissolving in water predetermined amounts of various components as shown in Tables 1 and 2 below.

[TABLE 1]

Example No.	1	2	3	4	5	6
Components:						
ZnSO <sub>4</sub> ·7H <sub>2</sub> O (Zn)	4.5	10.0	13.0	2.0	9.0	3.0
NH <sub>4</sub> HF <sub>2</sub> (F)	1.4	5.1	-	-	0.7	0.7
HF (55%) (F)	-	-	6.3	0.6	-	-
NiCl <sub>2</sub> ·6H <sub>2</sub> O (Ni)	-	-	-	-	0.8	-
CuCl (Cu)	-	-	-	-	-	6.4 ppm
FeCl <sub>3</sub> (Fe)	-	-	3.6	1.1	-	-
AgNO <sub>3</sub> (Ag)	-	-	-	-	-	-
PdCl <sub>3</sub> (Pd)	-	-	-	-	-	-
Citric Acid	-	-	-	-	-	-
Tartaric Acid	-	-	-	-	-	-
Gluconic Acid	-	-	-	-	-	-
Surfactant	-	-	-	-	-	-
pH	3.0	3.0 <sup>*1</sup>	2.0 <sup>*1</sup>	3.0 <sup>*1</sup>	3.0	4.0

[0035]

[TABLE 2]

Example No.	7	8	9	10
Components:				
ZnSO <sub>4</sub> ·7H <sub>2</sub> O (Zn)	1.2	7.5	3.0	1.2
NH <sub>4</sub> HF <sub>2</sub> (F)	0.7	-	0.7	-
HF (55%) (F)	-	7.5	-	1.5
NiCl <sub>2</sub> ·6H <sub>2</sub> O (Ni)	0.2	-	-	-
CuCl (Cu)	64 ppm	64 ppm	-	-
FeCl <sub>3</sub> (Fe)	-	-	-	-
AgNO <sub>3</sub> (Ag)	-	-	1.3 ppm	-
PdCl <sub>3</sub> (Pd)	-	-	-	3 ppm
Citric Acid	-	20	-	-
Tartaric Acid	-	-	3.0	-
Gluconic Acid	-	-	-	1.0
Surfactant	-	-	0.2	0.5
pH	3.0	1.5 <sup>*2</sup>	3.0	3.0 <sup>*1</sup>

[0036] The numerical values (amounts to be blended) for material compounds in the tables are concentrations (g/L, or  $\times 10^{-3}$  g/L for those indicated as ppm) in terms of fluorine (F) or metal elements. The surfactant used was an ethylene oxide adduct of nonyl phenol ("Emulgen 911" from Kao Corporation; cloudy point: 74°C). In the tables, "\*1" and "\*2" in the pH section indicate that pH was adjusted with an aqueous solution of caustic soda and an aqueous ammonia, respectively.

[0037]

[COMPARATIVE EXAMPLES 1 AND 2] Comparative zincate treatment solutions were prepared by dissolving in water various components as shown in Table 3 below. In Table 3, the amounts of components are shown in g/L.

[TABLE 3]

Comparative Example No.	1	2
Components:		
NaOH	150 g/L	500 g/L
ZnO	18	40
Rochelle Salt	20	30
FeCl <sub>3</sub>	8	-
CuSO <sub>4</sub> ·5H <sub>2</sub> O	-	12
pH		

?

[0038]

[EXAMINATION 1] Block-shaped aluminum materials and aluminum thin films were immersed in the zinc substitution solutions obtained in Examples 1-10 and the reference zinc substitution solutions (zincate treatment solutions) of Comparative Examples 1 and 2 under predetermined temperature conditions for predetermined amounts of time, thus subjecting the aluminum material surfaces to a zinc substitution treatment. Each obtained zinc-substituted aluminum was evaluated with respect to the uniformity of zinc substitution and the adhesiveness to the material.

[0039] The results are shown in Table 4 below, along with immersion conditions (temperature and time).

[TABLE 4]

Example No.	Examples					
	1	2	3	4	5	6
Treatment Temp (°C)	20	30	30	25	30	40
Treatment Time (sec)	50	60	60	120	60	360
Uniformity						
Block-Shaped Aluminum	Present	Present	Present	Present	Present	Present
Aluminum Thin Film	Present	Present	Present	Present	Present	Present
Adhesiveness						
Block-Shaped Aluminum	100/100	100/100	100/100	100/100	100/100	100/100
Aluminum Thin Film	100/100	100/100	100/100	100/100	100/100	100/100

Example No.	Examples				Comparative Examples	
	7	8	9	10	1	2
Treatment Temp (°C)	35	35	20	40	20	20
Treatment Time (sec)	30	25	120	50	30	30
Uniformity						
Block-Shaped Aluminum	Present	Present	Present	Present	Absent	Absent
Aluminum Thin Film	Present	Present	Present	Present	Unsubsti- tutable	Unsubsti- tutable
Adhesiveness						
Block-Shaped Aluminum	100/100	100/100	100/100	100/100	80/100	65/100
Aluminum Thin Film	100/100	100/100	100/100	100/100	Unsubsti- tutable	Unsubsti- tutable

[0040] It can be seen from Table 4 that with the use of the zinc substitution solution of the present invention, the zinc-substituted coat does not have non-uniformity, hence desirable uniformity, and has desirable adhesive strength, whether a block-shaped aluminum or an aluminum thin film is used as the aluminum material. In contrast, as shown in the comparative examples, with the conventional zincate treatment solution, a single immersion of a block-shaped aluminum results in non-uniformity and only gives a coat with insufficient adhesive strength, and with an aluminum thin film, the material aluminum entirely dissolves in the treatment solution and it is obviously not possible to form a zinc-substituted coat.

[0041]

[EXAMPLE 11] A JIS6063 aluminum plate material, which had in advance been subjected to degreasing, alkaline etching and desmutting with nitric acid, was immersed in a zinc substitution solution of the present invention as shown in Example 8, while being stirred, for 30 seconds at 35°C to thereby form a zinc-substituted coat.

[0042] Then, the obtained plate material is immersed in an electroless nickel plating bath "Topnicolon BL" from Okuno Chemical Industries Co., Ltd. for 30 minutes at 90°C to thereby form a nickel plating coat on the zinc-substituted coat, and is further subjected to nickel electroplating at a cathode current density of 2-4 A/dm<sup>2</sup> using a nickel electroplating bath (Watts bath) with a brightener added thereto, thus forming a nickel coat having a thickness of 10  $\mu\text{m}$ .

[0043] Chromium electroplating (cathode current density: about 20 A/dm<sup>2</sup>) in a sargent bath to a thickness of about 0.1  $\mu\text{m}$  was further performed on the obtained nickel coat.

[0044] Thus, there was obtained an aluminum plate having formed thereon a uniform plating coat having a desirable gloss and a desirable corrosion resistance.

[0045]

[EXAMPLE 12] An alkaline developable dry film (SUNFORTAQ5036 Dry Film from Asahi Kasei Corporation) was laminated, while being heated, onto a substrate with an aluminum coat having a thickness of 0.7  $\mu\text{m}$ , which had been obtained by vapor-depositing aluminum on a 99% alumina ceramic substrate.

[0046] Then, the product was exposed while masking portions that will eventually be needed, and the exposed portions were removed by developing the product with a 1% aqueous solution of sodium carbonate to thereby exposing the aluminum coat in



the unmasked portions.

[0047] The obtained substrate with the partially exposed aluminum coat was immersed in a zinc substitution solution of the present invention prepared as shown in Example 7 for 30  
5 seconds at 30°C to thereby form a zinc-substituted coat having a thickness of about 0.3  $\mu\text{m}$  on the exposed portions.

[0048] The product was further immersed in an acidic electroless nickel plating bath "ICP Nicolon USD" from Okuno Chemical Industries Co., Ltd. for 15 minutes at 85°C to  
10 thereby form a nickel-phosphorus coat having a thickness of about 3  $\mu\text{m}$  on the zinc-substituted coat.

[0049] Lastly, the obtained treatment substrate was immersed in a substitution-type electroless gold plating solution "Muden Noble AU" (having neutral pH) from Okuno Chemical  
15 Industries Co., Ltd. for 15 minutes at 65°C to thereby form a gold-substituted coat having a thickness of about 0.5  $\mu\text{m}$  on the nickel-phosphorus coat, after which the dry film and the aluminum thin film in the masked portions were peeled off by using a 3% aqueous solution of caustic soda with the obtained  
20 plating coat as a mask, thus obtaining an alumina ceramic substrate having an aluminum-nickel-gold coat as a desirably patterned conductive circuit.